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Barium isotope fractionation during experimental formation of the double carbonate $BaMn[CO_3]_2$ at ambient temperature

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In this study, we present the first experimental results for stable barium (Ba) isotope ($^{137}Ba/^{134}Ba$) fractionation during low-temperature formation of the anhydrous double carbonate $BaMn[CO_3]_2$. This investigation is part of an ongoing work on Ba fractionation in the natural barium cycle. Precipitation at a temperature of 21 ± 1°C leads to an enrichment of the lighter Ba isotope described by an enrichment factor of -0.11 ± 0.06‰ in the double carbonate than in an aqueous barium-manganese(II) chloride/sodium bicarbonate solution, which is within the range of previous reports for synthetic pure $BaCO_3$ (witherite) formation.

Keywords: ambient temperature; barium-134; barium-137; barium-manganese(II) double carbonate; isotope effects; precipitation experiment

1. Introduction

Fractionation processes for non-traditional stable isotopes are among the most evolving isotope research disciplines of the past decade [1]. Here, we report on new results in a developing and exciting very recent field: the fractionation of stable barium (Ba) isotopes [2].

Ba occurs essentially as a substitute for potassium in common constituents of rocks, such as feldspars, or in discrete Ba-bearing minerals in ore deposits in the continents [3]. Weathering in the continents leads to the release and further transport of dissolved and particulate Ba to the ocean [3]. In the water column, dissolved Ba shows a nutrient-type behaviour [4], with a relatively short residence time of about 11 kyr [5]. In sediments, discrete Ba-bearing minerals such as barite ($BaSO_4$) and witherite ($BaCO_3$) may be formed [6–11]. Another source of oceanic Ba is the hydrothermal solution that leads to the formation of Ba minerals in the mineral matrix of

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black and white smokers. Ba not only forms own minerals but may also substitute into the lattice of other important biogenic and authigenic minerals, such as calcite or aragonite [12,13]. The different biogeochemical pathways of Ba transport and reaction and the temporal or permanent burial of Ba in solid phases, in particular, under low-temperature conditions, are still not fully understood [14,15].

Therefore, based on the pioneering work of Nier [16] and Eugster *et al.* [17], stable Ba isotope ($^{137}Ba/^{134}Ba$) fractionation has recently been introduced as a new isotope proxy for the interpretation of reactions in the biogeochemical cycle of Ba [2]. In this study, it is shown that measurable differences exist between natural Ba minerals of different origins, indicating that chemical, physical, and/or biological fractionation processes for Ba isotopes do occur [2]. Since possible biological interactions and inorganic processes, such as mineral precipitation, complexation, diffusion, and/or sorption–desorption, are processes that potentially may induce mass-dependent variations in the Ba isotope composition of aqueous and solid phases, an accurate application of this new isotope tool on a mechanistic level requires a careful calibration of fractionation processes in experimental studies. Besides the more common minerals, the Ba-bearing double carbonate norsethite ($BaMg[CO_3]_2$) forms in a large variety of environments, for example, in sediments, hydrothermal and metamorphic settings, and carbonatites [18–22]. Norsethite is of particular interest because of its structural similarity to the rock-forming mineral dolomite ($CaMg[CO_3]_2$) [23]. Experimental evidence exists for the stability of $BaMn[CO_3]_2$ under a wide range of temperature and pressure conditions [24–26]. This carbonate is isostructural with norsethite [24,25,27]. In the present study, we present results on stable Ba isotope fractionation during the formation of the double carbonate $BaMn[CO_3]_2$ at ambient temperature. There are first hints for the occurrence of this carbonate in nature; however, it is expected that future (re)search will be successful in other suboxic and anoxic environments, essentially sulphate-free natural ones [25].

2. Materials and methods

The double carbonate $BaMn[CO_3]_2$ was synthesised at ambient temperature (21°C ± 1; 1 atm total pressure), as described earlier [25], from an aqueous solution that was initially 0.17 M in barium/manganese(II) chloride and 0.28 M in sodium bicarbonate. In the experiment, deionised water in a DURAN glass bottle was deoxygenated with an inert gas (N_2) and p.a.-grade Merck chemicals (in the order: $NaHCO_3$, $BaCl_2 \cdot 2H_2O$, and $MnCl_2 \cdot 4H_2O$) were subsequently dissolved in the agitated solution under a continuous stream of nitrogen gas. The mother solution and precipitate were then allowed to react for 10 days in a closed bottle. At the end of the experiment, the pH was measured with an ion-selective electrode (Mettler Toledo InLab Basics electrode and Schott handylab pH11 meter), and the precipitate was immediately separated from the experimental solution via membrane filtration (0.45 μm diameter pore widths), washed with deionised water, and dried in an oven at 60 °C. SEM-EDX analysis confirmed the 1:1 stoichiometry, and further powder X-ray diffraction and micro-Raman and FTIR spectroscopy confirmed the formation of a well-crystalline stoichiometric double carbonate [25]. The double carbonate was accompanied by co-precipitated rhodochrosite ($MnCO_3$). An aliquot of the aqueous experimental solution was acidified (p.a.-grade HNO_3) and the concentrations of the dissolved cations were measured after appropriate dilution by ICP-OES (Thermo, iCAP 6300 Duo) with accuracy and precision better than 3 and 6 %, respectively [28]. At the end of the experiment, the pH was 5.9 and the dissolved Ba/Mn ratio was about 16. For stable isotope analysis, the $BaCl_2$ used in the experiments was dissolved in deionised water, whereas the carbonate precipitate was dissolved in distilled 2.5 M hydrochloric acid. For multi-collector (MC)-ICP-MS measurements, aliquots of the mother solution were strongly diluted with 0.5 M HNO_3 to a Ba concentration of 0.25 ppm.

Furthermore, the mixtures of dissolved Mn nitrate and the Ba reference standard ($Ba(NO_3)_2$ solution, described below) with different Mn/Ba ratios were prepared to evaluate potential matrix effects resulting from the dissolved Mn^{2+} originating from the solid carbonate. A Ba double spike (masses 130 and 135) was added to the aliquots of the solutions. Subsequently, the homogenised solutions were evaporated and re-dissolved in 0.5 M HNO_3. Stable isotope measurements were performed on a double focusing Nu instrument® MC-ICP-MS equipped with 12 fixed Faraday cups (and three ion counters) in static mode as described in detail in [2]. Before analyses, the plasma was run for at least 2 h to achieve the stable measurement conditions. Ba masses 137 and 134 were selected as two of the seven natural Ba isotopes. ^{129}Xe and ^{131}Xe were selected to monitor Xe interferences on Ba. Xe correction was applied to the Ba masses 130 and 134. Generally, relative ^{130}Xe interferences on ^{130}Ba are less than 0.06 %. Xe correction was tested to be sufficiently precise [2]. Tellurium can cause isobaric interferences on ^{130}Ba. However, there is no source for Te in the experiments. Mass 128 (Te and Xe) was monitored by ion counting. After Xe interference correction, no detectable signal remained. Data acquisition comprised 3–4 blocks of 10 cycles per measurement (corresponding to 8–12 min). The measured solutions contained approximately 0.23 ppm of the component. Measurements consume about 1 ml of the solution, thus the total Ba amount needed was 230 ng. The Ba blank was constantly <0.04 ng. As outlined in detail earlier [2], the four stable Ba isotopes chosen for the double spike (masses 130 and 135) and the analysis of isotope partitioning (masses 134 and 137) were selected to suit the present MC-ICP-MS and also possible future TIMS analyses.

The measured Ba isotope ratios are given according to

$$\delta^{137/134}\mathrm{Ba}[‰] = \left(\frac{(^{137}\mathrm{Ba}/^{134}\mathrm{Ba})_{\mathrm{sample}}}{(^{137}\mathrm{Ba}/^{134}\mathrm{Ba})_{\mathrm{standard}}} - 1 \right) \times 1000$$

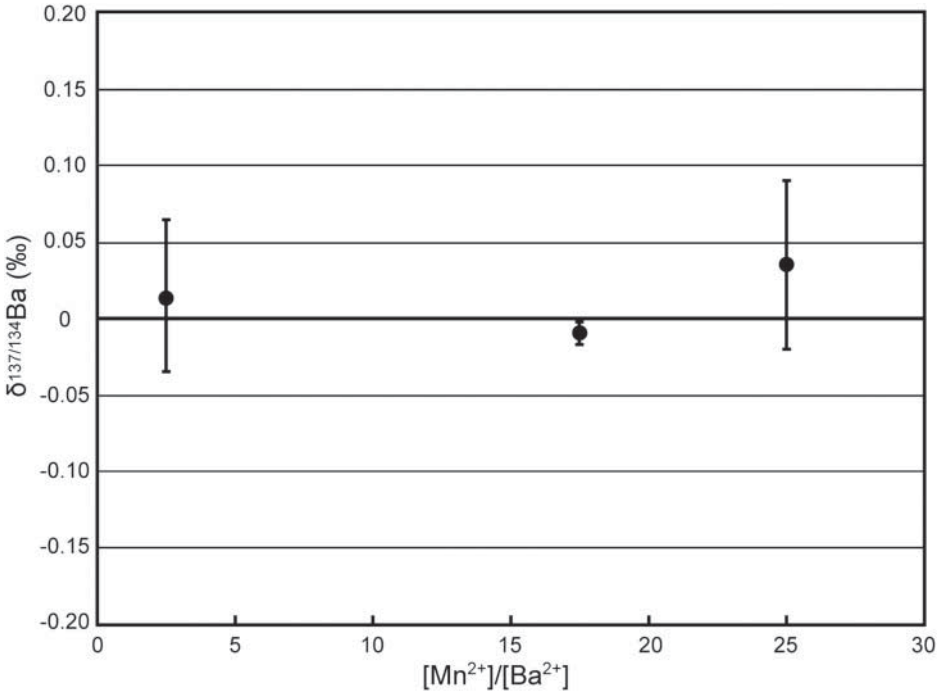

Figure 1. $\delta^{137/134}$Ba (‰) plotted versus the atomic manganese: Ba ratio of the solutions of the $Ba(NO_3)_2$ standard spiked with different Mn^{2+} concentrations. The data indicate that there is no measurable matrix effect imposed by the Mn^{2+} present in the solutions. The precipitated carbonate had an Mn^{2+}/Ba^{2+} ratio of about 3.

relative to a $Ba(NO_3)_2$ standard solution. The international IAEA standards IAEA-SO-5 and IAEA-SO-6 and IAEA-CO-9 have $\delta^{137/134}$Ba values identical within the errors to this solution [2]. The external reproducibility (2σ) of the standard solutions was better than $<0.1‰$. To achieve the resolution necessary for the present study, each solution was measured at least twice, and the 2σ error was calculated. No significant matrix effects from Mn^{2+} could be observed (Figure 1).

3. Results and discussion

For the formation pathway of $BaMn[CO_3]_2$ at 21°C from aqueous solutions, we suggest a replacement scenario, according to

$$Mn^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow MnCO_3 \downarrow \quad (1)$$

and

$$MnCO_3 + Ba^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow BaMn[CO_3]_2 \downarrow . \quad (2)$$

Also, direct precipitation of the double carbonate from the aqueous solutions cannot be ruled out. The pathway will depend on the initial boundary conditions (e.g. Ba/Mn ratios). For instance, for experiments on carbonate precipitation from mixed Mg-bearing solutions, Böttcher [29] described the alteration of an X-ray amorphous gel to crystalline $BaMg[CO_3]_2$.

The formation of the double carbonate was accompanied by an enrichment of the lighter Ba isotope in the solid phase than in the aqueous solution (Table 1). During the experiment, $BaMn[CO_3]_2$ was formed besides $MnCO_3$ (rhodochrosite). The large Ba cation should not be incorporated as a solid–solution component of $MnCO_3$ exceeding trace amounts [11]. In agreement with predictions, only very minor Ba was observed in the co-precipitated rhodochrosite using SEM-EDX [2], which may be caused by Ba attached to the surface of $MnCO_3$ or some intergrowths of $MnCO_3$ with the double carbonate. No indication of a co-precipitation of pure orthorhombic $BaCO_3$ was found using Rietfeld refinement of powder X-ray diffraction patterns, Raman and FTIR spectroscopy, and fresh oven-dried precipitates [2]. Therefore, the double carbonate is considered as the sole sink for Ba, and the change in aqueous Ba concentrations can be used to derive an isotope enrichment factor from the experimental results. Considering an isotopically closed system [30], the Ba isotope enrichment factor between the double carbonate and the aqueous solution is defined by a Rayleigh equation [31]:

$$\varepsilon[‰] = -\frac{(\delta^{137/134}Ba_{BaMn[CO_3]_2} - \delta^{137/134}Ba_{Ba^{2+},aq^\circ})}{(f \ln f)/(1-f)}. \quad (3)$$

The $\delta^{137/134}Ba_{BaMn[CO3]2}$ and $\delta^{137/134}Ba_{Ba^{2+},aq^\circ}$ values are the time-integrated solid-phase composition and the initial isotope composition of the aqueous solution, respectively. f is the residual fraction of Ba^{2+} remaining in the solution. The application of Equation (1) to the data given in

Table 1. Isotope composition ratio of barium chloride used to prepare the initial aqueous Ba solution and versus the precipitated $BaMn[CO_3]_2$.

Sample	$\delta^{137/134}$Ba (‰)
$BaCl_2 \cdot 2H_2O$	-0.01 ± 0.01 ($n = 2$)[a]
$BaMn[CO_3]_2$	-0.09 ± 0.05 ($n = 3$)

Notes: n, number of measurements. The probability that the $BaCl_2 \cdot 2H_2O$ and $BaMn[CO_3]_2$ data represent a single population is below 10 % (based on t-test).
[a]From [2].

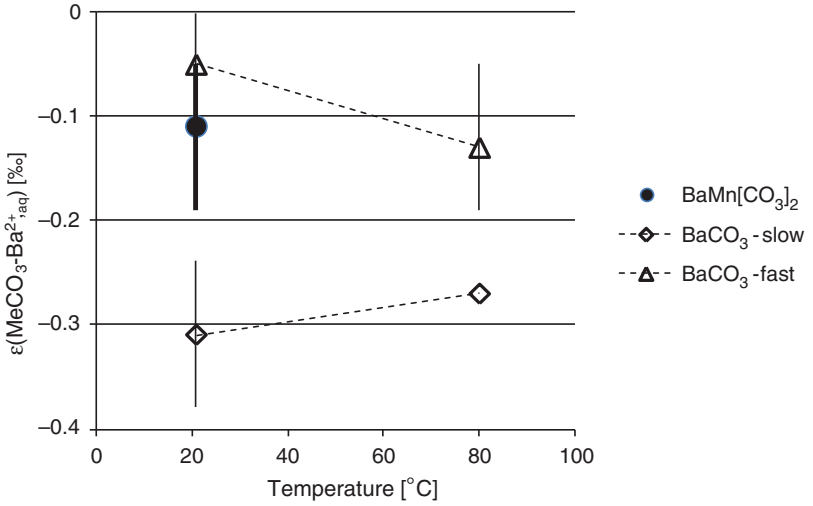

Figure 2. Ba isotope enrichment factors for the experimental precipitation of orthorhombic $BaCO_3$ (witherite) from aqueous solutions as a function of estimated precipitation conditions and temperature [2] compared with the results of this study on the double carbonate $BaMn[CO_3]_2$.

Table 1 with an observed f value of 0.51 yields an isotope enrichment factor of $-0.11 \pm 0.06‰$ (Figure 2).

It is evident that Ba isotopes are fractionated during the precipitation of anhydrous carbonate solids, enriching the lighter isotope in the solid than in the aqueous solution and that the magnitude is not constant for different boundary conditions. Regarding experiments forming pure orthorhombic $BaCO_3$ from Na-bicarbonate solutions (Figure 2), the results obtained for the double carbonate are lower in magnitude than those obtained for slowly precipitated witherite, but closer to the results obtained for witherite precipitation at relatively fast rates. This may indicate that under the chosen experimental conditions using aqueous bicarbonate solutions, the formation rate of the double carbonate is between those applied previously for $BaCO_3$. However, besides the precipitation rate, the mineral-specific fractionation factor and/or the speciation in the aqueous solution may also influence isotope discrimination. As noted earlier [2,32], the divalent Ba cations are hydrated in aqueous solution and may also form ion pairs with the bicarbonate and carbonate ions. Therefore, differences in the pH values of specific experiments may have influenced the concentrations of available ligands in the solution, but also at the solution–solid interface. Hofmann *et al.* [33], for instance, suggested an impact of ion desolvation on kinetic metal isotope fractionation, a process that certainly will be influenced by the composition of the aqueous solution. The first experimental data on witherite and barite formation in the presence of methanol modifying the solvation state of the ions and solid surface [32] actually indicate a small impact on Ba isotope discrimination (Böttcher *et al.*, unpublished). However, the precipitation rate may have been influenced under these conditions as well [32]. Further work will have to determine the role of isotope discrimination during the reaction progress as well as boundary conditions such as temperature, solution concentrations, and precipitation rate. As soon as the calibrations of isotope discriminations have been carried out, the degree of isotope discrimination into Ba-bearing solids may be used to deduce the conditions of carbonate formation.

It should be noted that our results on Ba isotope fractionation support previous investigations on other earth alkaline isotope systems. Calcium, magnesium, and strontium isotope effects, for instance, have been observed previously during calcite and aragonite formation from aqueous solutions [34–37]. As in the case of Ba, it was observed experimentally and in the field that the

lighter isotopes are enriched in the solids than in the dissolved cations and that the magnitude depends on the precipitation rate and solid-phase structure. This preferential incorporation of the lighter isotopes has been interpreted as a result of dehydration of the cation, reaction kinetics, or an entrapment of the lighter isotope at the carbonate surface [36,38].

4. Conclusion

In the present study, it was found that the formation of $BaMn[CO_3]_2$ from aqueous solution at 21°C and 1 atm total pressure gave an isotope enrichment factor within the range of previous reports for the precipitation of pure witherite from carbonate- or bicarbonate-bearing solutions at the same temperature. Further work focuses on the processes responsible for Ba isotope discrimination and the effects of physico-chemical boundary conditions and the actual formation pathway on the basic mechanisms. It was found and predicted for Ca, Mg, and Fe(II) isotopes in different carbonate systems [1,39] that, besides factors such as reaction kinetics, the composition and crystal chemistry of the solid influence isotope partitioning – systematics that will be investigated now for Ba isotopes in more detail.

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References

[1] C.A. Johnson, B.L. Beard, and F. Albarède, editors, *Geochemistry of Non-Traditional Stable Isotopes*, Reviews in Mineralogy & Geochemistry, Vol. 55 (Mineralogical Society of America, Washington, 2004), 454 pp.

[2] K. von Allmen, M.E. Böttcher, E. Samankassou, and T.F. Nägler, Barium Isotope Fractionation in the Global Barium Cycle: First Evidence from Barium Minerals and Precipitation Experiments, *Chem. Geol.* **277**, 70 (2010).

[3] H. Puchelt, Zur Geochemie des Bariums im exogenen Zyklus, *Sitzungsber. Heidelb. Akad. Math. Wiss. Nat. Kl.* **4**, 85 (1967).

[4] L.H. Chan, J.M. Edmond, R.F. Stallard, W.S. Broecker, Y.C. Chung, R.F. Weiss, and T.L. Ku, Radium and Barium at GEOSECS Stations in the Atlantic and Pacific, *Earth Planet. Sci. Lett.* **32**, 258 (1976).

[5] J.M. Edmond, C. Measures, R.E. McDuff, L.H. Chan, R. Collier, B. Grant, L.I. Gordon, and J.B. Corliss, Ridge Crest Hydrothermal Activity and the Balances of the Major and Minor Elements in the Ocean – Galapagos Data, *Earth Planet. Sci. Lett.* **46**, 1 (1979).

[6] T.M. Church, Marine Barite, in *Marine Minerals*, edited by R.G. Burns, Reviews in Mineralogy, Vol. 6 (Mineralogical Society of America, Washington, 1979), pp. 175–209.

[7] F.X. Gingele and A. Dahmke, Discrete Barite Particles and Barium as Tracers of Paleoproductivity in South Atlantic Sediments, *Paleoceanography* **9**, 151 (1994).

[8] M.E. Torres, H.J. Brumsack, G. Bohrmann, and K.C. Emeis, Barite Fronts in Continental Margin Sediments: A New Look at Barium Remobilization in the Zone of Sulfate Reduction and Formation of Heavy Barites in Authigenic Fronts, *Chem. Geol.* **127**, 125 (1996).

[9] A. Paytan and E.M. Griffith, Marine Barite: Recorder of Variations in Ocean Export Productivity, *Deep-Sea Res. Part II–Top. Stud. Oceanogr.* **54**, 687 (2007).

[10] N. Riedinger, S. Kasten, J. Gröger, C. Franke, and K. Pfeifer, Active and Buried Barite Fronts in Sediments from the Eastern Cape Basin, *Earth Planet. Sci. Lett.* **241**, 876 (2006).

[11] M.E. Böttcher and M. Dietzel, Metal-Ion Partitioning during Low-Temperature Precipitation and Dissolution of Anhydrous Carbonates and Sulfates, *EMU Notes Mineral.* **10**, 139 (2010).

[12] N.E. Pingitore and M.P. Eastman, Barium Partitioning During the Transformation of Corals from Aragonite to Calcite, *Chem. Geol.* **48**, 183 (1985).

[13] G. Langer, G. Nehrke, S. Thoms, and H. Stoll, Barium Partitioning in Coccoliths of *Emiliania huxleyi*, *Geochim. Cosmochim. Acta* **73**, 2899 (2009).

[14] J. McManus, W.M. Berelson, G.P. Klinkhammer, K.S. Johnson, K.H. Coale, R.F. Anderson, N. Kumar, D.J. Burdige, D.E. Hammond, H.J. Brumsack, D.C. McCorkle, and A. Rushdi, Geochemistry of Barium in Marine Sediments: Implications for Its Use as a Paleoproxy, *Geochim. Cosmochim. Acta* **62**, 3453 (1998).

[15] R.S. Ganeshram, R. François, J. Commeau, and S.L. Brown-Leger, An Experimental Investigation of Barite Formation in Seawater, *Geochim. Cosmochim. Acta* **67**, 2599 (2003).

[16] A.O. Nier, The Isotopic Constitution of Strontium, Barium, Bismuth, Thallium and Mercury, *Phys. Rev.* **54**, 275 (1938).

[17] O. Eugster, F. Tera, and G.J. Wasserburg, Isotopic Analyses of Barium in Meteorites and in Terrestrial Samples, *J. Geophys. Res*. **74**, 3897 (1969).

[18] M.E. Mrose, E.C.T. Chao, J.J. Fahey, and C. Milton, Norsethite, $BaMg(CO_3)_2$, a New Mineral from the Green River Formation, Wyoming, *Amer. Mineral.* **46**, 420 (1961).

[19] J.G.D. Steyn and M.D. Watson, Notes on a New Occurrence of Norsethite, *Am. Mineral.* **52**, 1770 (1967).

[20] N. Sundius and R. Blix, Norsethite from Långban, *Arkiv. Mineral. Geol.* **4**, 277 (1965).

[21] R.G. Platt and A.R. Woolley, The Carbonatites and Fenites of Chipman Lake, Ontario, *Can. Mineral.* **28**, 241 (1990).

[22] N. Zidarov, O. Petrov, M. Tarassov, Z. Damyanov, E. Tarassova, V. Petkova, Y. Kalvachev, and Z Zlatev, Mn-Rich Norsethite from the Kremikovtsi Ore Deposit, Bulgaria, *N. Jb. Mineral. Abh.* **186**, 321 (2009).

[23] F. Lippmann, *Sedimentary Carbonate Minerals* (Springer, Heidelberg/New York, 1973), 228 pp.

[24] L.L.Y. Chang, Synthesis of $MBa(CO)_3$ Compounds, *Am. Mineral.* **49**, 1142 (1964).

[25] M.E. Böttcher, H.S. Effenberger, P.-L. Gehlken, G. Grathoff, B. Schmidt, P. Geprägs, R. Bahlo, O. Dellwig, T. Leipe, V. Winde, A. Deutschmann, A. Stark, D. Gallego-Torres, and F. Martinez-Ruiz, $BaMn[CO_3]_2$– A Previously Unrecognized Double Carbonate in Low-Temperature Environments: Structural, Spectroscopic, and Textural Tools for Future Identification, *CdE–Geochemistry*, published online 9 February 2012.

[26] B. Schmidt, P.-L. Gehlken, and M.E. Böttcher, The Vibrational Spectra of $BaMn[CO_3]_2$, *Eur. J. Mineral*., submitted.

[27] H. Effenberger and J. Zemann, Single Crystal X-Ray Investigation of Norsethite, $BaMg(CO_3)_2$: One More Mineral with an Aplanar Carbonate Group, *Z. Kristall.* **171**, 275 (1985).

[28] N. Kowalski, O. Dellwig, M. Beck, M. Grunwald, T. Badewien, H.J. Brumsack, J.E.E. van Beusekom, and M.E. Böttcher, A Comparative Study of Manganese Dynamics in the Water Column and Sediments of Intertidal Systems of the North Sea, *Estuar. Coast. Shelf Sci*. **100**, 3 (2012).

[29] M.E. Böttcher, Stable Isotope Fractionation during Experimental Formation of Norsethite ($BaMg[CO_3]_2$): A Mineral Analogue of Dolomite, *Aquat. Geochem.* **6**, 201 (2000).

[30] M. Hartmann and H. Nielsen, δ^{34}S Values in Recent Sea Sediments and Their Significance Using Several Sediment Profiles from the Western Baltic Sea (M.E. Böttcher and J. Hoefs, Sulphur Tales: A Tribute on the Occasion of the 90th Birthday of Heimo Nielsen), *Isot. Environ. Health Stud.* **48**, 7 (2012).

[31] A. Mariotti, J.C. Germon, P. Hubert, P. Kaiser, R. Létolle, A. Tardieux, and P. Tardieux, Experimental Determination of Nitrogen Kinetic Isotope Fractionation: Some Principles; Illustration for the Denitrification and Nitrification Processes, *Plant Soil* **62**, 413 (1981).

[32] M. Kowacz, C.V. Putnis, and A. Putnis, The Effect of Cation:Anion Ratio in Solution on the Mechanism of Barite Growth at Constant Supersaturation: Role of the Desolvation Process on the Growth Kinetics, *Geochim. Cosmochim. Acta* **71**, 5168 (2007).

[33] A.E. Hofmann, I.C. Bourg, and D.J. de Paolo, Ion Desolvation as a Mechanism for Kinetic Isotope Fractionation, *Mineral. Mag.* **75**, 1035 (2011).

[34] J. Fietzke and A. Eisenhauer, Determination of Temperature-Dependent Stable Strontium Isotope (^{88}Sr/^{86}Sr) Fractionation via Bracketing Standard MC-ICP-MS, *Geochem. Geophys. Geosyst.* **7**, Q08009 (2006), doi:10.1029/2006GC0012432006.

[35] N. Gussone, A. Eisenhauer, A. Heuser, M. Dietzel, B. Bock, F. Böhm, H.J. Spero, D.W. Lea, J. Bijma, and T.F. Nägler, Model for Kinetic Effects on Calcium Isotope Fractionation (δ^{44}Ca) in Inorganic Aragonite and Cultured Planktonic Foraminifera, *Geochim. Cosmochim. Acta* **67**, 1375 (2003).

[36] A. Immenhauser, D. Buhl, A. Niedermayr, D. Riechelmann, M. Dietzel, and U. Schulte, Magnesium-Isotope Fractionation during Low-Mg-Calcite Precipitation in a Limestone Cave – Field Study and Experiments, *Geochim. Cosmochim. Acta* **74**, 4346 (2010).

[37] F. Wombacher, A. Eisenhauer, F. Böhm, N. Gussone, M. Regenberg, W.-C. Dullo, and A. Rüggeberg, Magnesium Stable Isotope Fractionation in Marine Biogenic Calcite and Aragonite, *Geochim. Cosmochim. Acta* **75**, 5797 (2011).

[38] J. Tang, M. Dietzel, F. Böhm, S. Köhler, and A. Eisenhauer, Sr^{2+}/Ca^{2+} and $^{44}Ca/^{40}Ca$ Fractionation during Inorganic Calcite Formation. II. Ca Isotopes, *Geochim. Cosmochim. Acta* **72**, 3733 (2008).

[39] J.R. Rustad, W.H. Casey, Q.-Z. Yin, E.J. Bylaska, A.R. Felmy, S. Bogatko, V.E. Jackson, and D.A. Dixon, Isotopic Fractionation of $Mg^{2+}_{(aq)}$, $Ca^{2+}_{(aq)}$, and $Fe^{2+}_{(aq)}$ with Carbonate Minerals, *Geochim. Cosmochim. Acta* **74**, 6301 (2010).